Direct Observation of Compositionally Homogeneous a -C:H Band-Gap-Modulated Superlattices

C. A. Davis,¹ S. R. P. Silva,² R. E. Dunin-Borkowski,¹ G. A. J. Amaratunga,² K. M. Knowles,¹ and W. M. Stobbs¹

¹*Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, United Kingdom*

²*Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, United Kingdom*

(Received 7 February 1995)

It is shown that amorphous hydrogenated carbon (a -C:H) band-gap-modulated superlattices can be observed by transmission electron microscopy. The layering proves to be well defined and it is demonstrated that changes in the band gap from 1.5 to 2.8 eV cannot be associated with ordered graphitic regions, in that crystalline regions larger than 0.5 nm are not observed. Differences in the amount of π bonding are found to lead to changes in the average atomic scattering factor. It is suggested that the changes in π bonding are associated with changes in local ordering that control the band gap.

PACS numbers: 68.65.+g, 61.14.-x, 61.16.Bg, 61.43.Dq

Superlattice structures consisting of alternate layers of lattice-matched crystalline materials with different band gaps are known to exhibit a variety of interesting and important quantum mechanical effects for sufficiently small layer widths [1]. Abeles and Tiedje [2] have shown that related effects can be observed in superlattices consisting of pairs of amorphous materials such as a -Si:H/ a -SiN:H. All of the band-gap-modulated superlattices of this class that have been studied to date have been heterogeneous systems in the sense that the high and low band-gap layers have been made of amorphous materials with substantially different chemical compositions.

Hydrogenated amorphous carbon (a -C:H) films made by RF plasma decomposition of low pressure hydrocarbon gases contain a mixture of tetrahedral (sp^3), trigonal (sp^2), and linear (sp^1) carbon bonding, as well as a significant fraction of incorporated hydrogen. The mechanical, optical, and electrical properties of these films can vary considerably depending on the deposition conditions [3]. In particular, the Tauc optical band gap [4] can be varied over the surprisingly large range of 1.2 to 4 eV simply by changing the power of the RF excitation [5]. This enables band-gap-modulated superlattice structures to be fabricated by sequentially depositing high and low band-gap a -C:H layers [6–8]. Since the alternate layers are both a -C:H, these superlattices are unusual in that the large band-gap modulation is obtained for a minimal change in the hydrogen content for the high density films examined here. Competing explanations of the origin of the large band-gap variation in such a material include significant changes in C-C or C-H bonding configurations [9], changes in the size of graphitic clusters [9], and changes in the distortion of ring structures [10].

In this Letter, transmission electron microscope (TEM) techniques are used to characterize the structure of a -C:H band-gap-modulated superlattices. The layers differ in their H contents by only 3 at. %. It is shown that the

superlattice can be imaged using the Fresnel contrast caused by small changes in density and bonding. Electron energy loss spectroscopy (EELS) and dark field TEM observations are used to characterize the valence electron density, bonding type, and structure. The relationship between the optical band gap and the structure of high density a -C:H films is discussed in the light of the above results.

The superlattice structures studied here are identical to those described by Silva *et al.* [8]. They were made by plasma enhanced chemical vapor deposition on clean (001) silicon substrates which were placed on an electrode held at 20 °C and driven at 13.56 MHz in a mixture of 8% CH₄ with 92% Ar at a pressure of 40 Pa. During growth the RF power was periodically altered under computer control between two values which gave dc self-bias voltages of –190 and –265 V. The nominal deposition rates at the two plasma powers were 0.4 and 0.5 nm s^{–1} respectively. On the basis of the equilibrium growth rates, the superlattices examined here were expected to consist of 10 low band-gap layers (–190 V bias) each 6 nm thick and 11 high band-gap layers (–265 V bias) each 10 nm thick. Silva *et al.* [8] have observed resonant tunneling and a blueshift in the optical absorption of these superlattices with decreasing layer thickness.

Prior to investigation of the superlattice structure, high and low band-gap single layer films grown under identical conditions to those used for the individual layers of the superlattice were examined. Data for the films are summarized in Table I. The optical band gaps were obtained using the Tauc [4] relationship and the hydrogen concentrations were determined from elastic recoil data analysis (ERDA) using 30 MeV Cl ions. It can be seen that there is a large difference in the optical properties, but only a small change in the hydrogen concentration. Approximately 0.3 at. % of both oxygen and nitrogen were found by ERDA in both films, but no other contaminants were detected. The single layer films were removed

TABLE I. Properties of single layer films deposited under identical conditions to the high and low band-gap layers in the superlattice.

Self-bias	-190 V	-265 V
Optical band gap	1.5 eV	2.8 eV
Hydrogen concentration	36 ± 2 at. %	33 ± 2 at. %
Plasmon energy	23.0 ± 0.1 eV	23.8 ± 0.1 eV
π bonds per carbon atom	0.87 ± 0.05	0.74 ± 0.05

from the silicon substrate using an HF/HNO₃ solution and characterized using a Gatan 666 EELS attached to a Philips CM30 TEM operated at 100 kV. The EELS energy resolution was 1.1 eV and a collection semiangle of 1 mrad was used for the plasmon energy measurements and 12 mrad otherwise. Table I shows the plasmon loss peak energies. The number of π bonds per carbon atom is also shown for each type of film, as obtained from the area of the $1s-\pi^*$ peak relative to that of the $1s-\sigma^*$ edge and normalized using a polycrystalline graphite standard [11]. Note that the common practice of expressing the amount of π bonding in terms of an sp^2 or sp^3 fraction is not used here since sp^1 bonding may be present [5].

Using the free-electron formula [12] and taking into account the measured hydrogen contents, the plasmon energies shown in Table I correspond to densities of approximately 1.75×10^3 and 1.9×10^3 kg m⁻³, the high band-gap film having a $(7 \pm 2)\%$ greater density than the low band-gap *a*-C:H. The plasmon energy of the whole multilayer structure was 23.7 ± 0.1 eV and the number of π bonds per carbon atom determined from the *K* edge was 0.8 ± 0.1 . Within experimental error, this value of the plasmon energy for the entire multilayer is what would be expected on the basis of a volume average value of the individual layers, taking into account the relative layer thicknesses, indicating that any effects due to interface structure are small. No edges other than that for carbon were detected, which is consistent with there being less than 1 at. % N and O contamination. The diffraction patterns of the single layer films and the multilayer exhibited diffuse rings that were qualitatively indistinguishable and consistent with an amorphous structure, the broad halo below 2.5 nm^{-1} being typical of *a*-C:H [13].

Cross-sectional TEM specimens were made from the multilayer structures by backgrinding and polishing the substrate to a thickness of about 0.1 mm prior to cleaving 90° wedges, which were mounted on copper supports and viewed edge-on in the TEM [14]. The method is rapid, avoids problems with contamination and ion bombardment-induced structural changes, and gives a known variation of thickness over a wide range. One drawback to the use of cleaved wedges for cross-sectional TEM is that the thin area is small, and so in this work several specimens were compared to ensure that

the results were reproducible. The 90° wedge cross-sections were examined in a Philips CM30 TEM operated at 300 kV and were oriented edge-on to the optic axis of the microscope using the known (001) orientation of the silicon substrate. Prolonged exposure to the 300 kV electron beam led to a gradual loss of contrast between the layers as a result of ionization and knock-on damage. Images were therefore obtained using a low electron current density and a total time in the beam which was a factor of 10 shorter than that required for beam damage to remove the layer contrast. Techniques requiring a high current density, such as the use of a small probe to acquire EEL spectra from the individual layers, were not attempted.

The superlattice structure proved to be viewable far from focus, as is demonstrated by the image in Fig. 1, in which the low band-gap layers (arrowed) are brighter than the high band-gap layers. It should be noted that the defocus value used is large (more than 50 times the Scherzer defocus) and that in-focus images show negligible contrast. The lack of contrast near zero defocus is consistent with the layers having approximately equal atomic number and similar amorphous structures. Far

FIG. 1. Bright field transmission electron microscope image of the *a*-C:H superlattice obtained with a 3 mrad objective aperture, 0.12 mrad convergence and $-6 \mu\text{m}$ defocus. The silicon substrate is at the bottom of the image and the wedge increases in thickness from right to left. The low band-gap layers are arrowed. Note that the true widths of the low band-gap layers are actually less than the apparent thickness deduced from the width of the brighter layers in this image (e.g., [15]).

from focus the layers are visible because of the Fresnel contrast caused by the small difference in the phase shift for electrons passing through the high and low band-gap layers. The fact that the low band-gap layers are bright in underfocused images indicates a smaller phase shift or, equivalently, a smaller forward scattering potential than the high band-gap layers [15]. In all of the specimens examined, the layers were parallel to the silicon substrate and approximately uniform in spacing. The superlattice period is 15 nm near the substrate, increasing to 18 nm over the first few layers, the increase in the deposition rate probably being caused by changes in the coupling of the RF power through the semi-insulating superlattice. The average period of the central seven layer pairs was measured to be 17.7 ± 0.9 nm, slightly larger than the expected value of 16 nm.

The full analysis of the Fresnel data obtained is presented elsewhere [16]. Twenty images from a through-focal series were digitized, and the known variation of specimen thickness with distance from the edge of the 90° wedge was used to obtain the layer contrast as a function of thickness. Extrapolation of the contrast to a thickness of 10 nm then minimized inelastic and multiple scattering effects. Images were calculated from a one-dimensional model of the forward scattering potential using measured values for microscope parameters such as the defocus and spherical aberration. The layer width as a function of defocus was well fitted for layer thicknesses of 5.3 ± 0.3 and 12.4 ± 0.5 nm. Comparison of these values with the layer thickness ratio of 0.60 ± 0.08 expected from the relative growth times suggests that the high band-gap layers have been enlarged at the expense of the low band-gap layers by 1.2 ± 0.8 nm. This is consistent with a densification of the top of the low band-gap layers by the more energetic plasma used to deposit the high band-gap layers, as predicted by subplantation growth models [17,18].

The calculated images gave an optimum fit to the contrast as a function of defocus for a difference in the forward scattering potential, V_0 , of $\Delta V_0 = 0.10 \pm 0.02$ V, with the low band-gap layers having the lower magnitude of forward scattering potential. This very small value for ΔV_0 is not consistent with the layer densities obtained from the measured plasmon energies, which would give the low band-gap layers a forward scattering potential 0.8 ± 0.2 V lower in magnitude than that of the high band-gap layers. X-ray photoelectron spectroscopy measurements [8] suggest a difference in space charge potential, and thus of the forward scattering potential, of no more than 0.2 V, so such an effect does not explain the small value of ΔV_0 observed. We therefore infer that the mean forward atomic scattering factor in the high band-gap layers must be some $(6 \pm 4)\%$ lower than that of the low band-gap layers. That is, the individual carbon atoms in the high band-gap layers on

average scatter more weakly at low angles than do those in the low band-gap layers.

The origin for the reduced level of Fresnel contrast that we have found lies in the fact that the low band-gap material has more π bonding than the high gap material, as we have inferred from our assessment of the C K edge for the two materials. The way in which the form of the electronic charge distribution can be expected to affect a scattering potential has been illustrated recently by O'Keeffe and Spence using Gaussian electron distributions [19]. They show that the forward atomic scattering potential seen by high energy electrons is very sensitive to bonding effects. For example, electrons located on average far away from the nucleus, as in π bonds, will have a disproportionately larger contribution to the mean forward atomic scattering factor than will electrons in sp^2 or sp^3 σ bonds located on average nearer the nucleus. The effect of this is that there will be a lower mean forward atomic scattering factor for an atom where there are 4 sp^3 σ bonds than for an atom where there are 3 sp^2 σ bonds and a π bond. As a consequence, for the amorphous materials we have examined, such effects would be expected to increase the magnitude of the forward scattering potential of the low band-gap material to a value closer to that of the high band-gap material than would otherwise have been expected in the absence of a difference in bonding in the two different types of layer.

The superlattice structure was further investigated using a JEOL 4000EX TEM with a point-to-point resolution of 0.16 nm, which was operated at 400 kV. High resolution bright field images showed no layer contrast and neither any crystalline nor ordered regions in the layers. A dark field image of the superlattice obtained at a mean scattering angle of 3.0 nm^{-1} with an objective aperture subtending 2.5 nm^{-1} is shown in Fig. 2. It can be seen that speckle contrast typical of an amorphous material dominates, with no discernible difference between the high and low band-gap layers. No differences in the dark field contrast of the layers were observed for mean scattering angles in the $1.0\text{--}4 \text{ nm}^{-1}$ range, which implies that there are no changes in either the medium range ordering [13] or in porosity. Bright field Fresnel images taken after dark field imaging retained layer contrast so that the lack of layer contrast in the dark field images was not due to damage by the 400 kV electrons.

The size of the dark field speckle observed in thin regions of the superlattice depended on the angular size of the objective aperture used, decreasing to 0.16 nm for an aperture 7.8 nm^{-1} in size. This behavior is consistent with the material being amorphous [20], and no evidence for the presence of any crystallinity was obtained. Graphitic regions larger than about 0.5 nm in size would have been clearly visible if they had been present.

FIG. 2. Dark field transmission electron microscope image of the a -C:H superlattice for a mean scattering angle of 3.0 nm^{-1} . The mean speckle size is 0.5 nm , consistent with the 0.49 nm Airy disk size of the aperture. The silicon substrate is at the bottom of the image and the wedge increases in thickness from right to left.

The superlattices described above form an interesting system for the comparison of high and low band-gap a -C:H. Here we have shown that the density and hydrogen content are almost the same and that there is a small change in the number of π bonds. The latter may be understood by recognizing that most of the bonding structures likely to be present (e.g., sp^1 chains, sp^2 even-membered rings or pairs, sp^3 sites) give states separated by more than 4 eV [9]. The lower band gaps usually observed in a -C:H can then be attributed to the presence of a minority of sites which contribute the states that form the band edge. The dark field results described above

rule out the suggestion that the band edge states are due to graphitic clusters $0.5\text{--}1.5 \text{ nm}$ in size [9]. The observed increase in π bonding as the band gap decreases suggests that π bonded sites may be responsible for the band-edge states, possibly in the form of disordered ring structures as recently proposed by Robertson [10].

The authors gratefully acknowledge useful discussions with Professor A. Howie, F.R.S., and financial support for this work from the U.K. Engineering and Physical Sciences Research Council.

-
- [1] *Synthetic Modulated Structures*, edited by L. L. Chang and B. C. Geissen (Academic Press, New York, 1985).
 - [2] B. Abeles and T. Tiedje, *Phys. Rev. Lett.* **51**, 2003 (1983).
 - [3] J. Robertson, *Adv. Phys.* **35**, 317 (1986).
 - [4] J. Tauc, R. Grigorovic, and A. Vancu, *Phys. Status Solidi* **15**, 627 (1966).
 - [5] S. R. P. Silva, G. A. J. Amaratunga, and C. P. Constantinou, *J. Appl. Phys.* **72**, 1149 (1992).
 - [6] V. I. Polyakov *et al.*, *Thin Solid Films* **212**, 226 (1992).
 - [7] K. K. Chan, S. R. P. Silva, and G. A. J. Amaratunga, *Thin Solid Films* **212**, 232 (1992).
 - [8] S. R. P. Silva *et al.*, *Jpn. J. Appl. Phys.* **33**, 6154 (1994).
 - [9] J. Robertson and E. P. O'Reilly, *Phys. Rev. B* **35**, 2946 (1987).
 - [10] J. Robertson (to be published).
 - [11] S. D. Berger *et al.*, *Ultramicroscopy* **28**, 43 (1988).
 - [12] R. F. Egerton, *Electron Energy Loss Spectroscopy in the Electron Microscope* (Plenum, New York, 1986), pp. 151–164.
 - [13] D. R. McKenzie *et al.*, *Thin Solid Films* **193/194**, 418 (1990).
 - [14] J. M. Cowley, *Acta. Crystallogr. Sect. A* **25**, 129 (1969).
 - [15] W. M. Stobbs and F. M. Ross, *NATO ASI, Ser. B, Vol. 203* (Plenum, London, 1989), p. 183; F. M. Ross and W. M. Stobbs, *Philos. Mag. A* **63**, 37 (1991).
 - [16] C. A. Davis *et al.* (to be published).
 - [17] Y. Lifshitz *et al.*, *Phys. Rev. B* **41**, 10468 (1990).
 - [18] J. Robertson, *Philos. Trans. R. Soc. London A* **342**, 277 (1993).
 - [19] M. O'Keeffe and J. C. H. Spence, *Acta. Crystallogr. Sect. A* **50**, 33 (1994).
 - [20] J. M. Gibson and A. Howie, *Chem. Scr.* **14**, 109 (1979).

FIG. 1. Bright field transmission electron microscope image of the *a*-C:H superlattice obtained with a 3 mrad objective aperture, 0.12 mrad convergence and $-6\text{ }\mu\text{m}$ defocus. The silicon substrate is at the bottom of the image and the wedge increases in thickness from right to left. The low band-gap layers are arrowed. Note that the true widths of the low band-gap layers are actually less than the apparent thickness deduced from the width of the brighter layers in this image (e.g., [15]).

FIG. 2. Dark field transmission electron microscope image of the *a*-C:H superlattice for a mean scattering angle of 3.0 nm^{-1} . The mean speckle size is 0.5 nm, consistent with the 0.49 nm Airy disk size of the aperture. The silicon substrate is at the bottom of the image and the wedge increases in thickness from right to left.